

Influence of the microporosity and surface chemistry of polymeric resins on adsorptive properties toward phenol

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Abstract

In this work, the effects of the microporosity and chemical surface of polymeric adsorbents on adsorptive properties of phenol were investigated. Textural parameters of four kinds of polymeric resins, namely AB-8, D4006, NKA-II and D16 resin, were separately measured by ASAP 2010. The surface chemistry of these polymeric resins was determined by means of inverse gas chromatography (IGC) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Static equilibrium adsorption experiments were carried out to obtain the isotherms of phenol on the polymeric resins. It was shown that NKA-II and AB-8 resin possessed relatively high BET surface areas and micropore volumes, while D4006 and D16 resin possessed comparatively low BET surface areas and micropore volumes. The results of IGC experiments revealed that NKA-II resin had extraordinary high specific component of the free energy of adsorption both for polar acetone and benzene probe, and thus extraordinary strong surface polarity compared to the other polymeric resins. It was also found that the isotherm of phenol on NKA-II was much higher than that on the other polymeric resins due to its strongest surface polarity and largest micropore volume among four kinds of resins. These experimental observations indicated that adsorption of phenol on the polymeric resins depended greatly on their microporosity and surface chemistry. The well-developed microporosity and the strong surface polarity would improve the adsorption of phenol on the polymeric resins.

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1. Introduction

Phenolic compounds including substituted phenols are common pollutants in wastewaters in the petroleum, coal conversion and other chemical processes. Almost all phenols are inherently toxic, and some are even considered to be carcinogenic [1]. Consequently, the removal or destruction of phenols from wastewaters is of great importance.

Current methods for the treatment of phenolic wastewater include biological degradation, chemical oxidation, membrane separation, solvent extraction, and adsorption on activated carbon. Due to their wide variations in porosity and surface chemistry, there has been a growing interest in devel-

oping polymeric adsorbents as an alternative to activated carbon for the selective removal of phenols from contaminated water [2–5]. When adsorption occurs between a polar adsorbate and an adsorbent, the surface chemistry of the adsorbent could be very important as well as its porous properties [6]. The aim of the present work is to investigate, experimentally, the effects of the microporosity and chemical surface of polymeric adsorbents on adsorptive properties toward phenol. The porous structure of four polymeric resins was determined by low-temperature nitrogen adsorption experiment. The chemical properties of the polymeric resins were studied by inverse gas chromatography (IGC) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Then the effects of physical and chemical properties of these polymeric resins on the adsorption of phenol would be discussed.

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2. Experimental

2.1. Resins and reagents

Four polymeric resins, AB-8, D4006, NKA-II and D16 resin, were purchased from the Chemical Plant of Nankai University (Tianjin, China). Diameters of the resins ranged from 0.3 to 1.0 mm. Prior to use, they were washed with deionized water several times to remove inorganic impurities like NaCl, followed by acetone to remove organic impurities, and then dried at 343 K in a vacuum for 3 h. The reagents used in this experiment were phenol, C₅–C₈ *n*-alkanes, benzene and acetone (analytical grade).

2.2. Nitrogen adsorption experiments

Nitrogen adsorption experiments, carried out at 77 K using an accelerated surface area and porosimeter system (ASAP 2010, Micromeritics), were used to determine the textural properties of all the polymeric resins. The BET surface area was calculated from the adsorption isotherms using the standard Brunauer–Emmett–Teller (BET) equation. The *t*-plot method was used to calculate the micropore volume. The pore size distributions (PSD) were determined using Density Functional Theory (DFT) based on statistical mechanics.

2.3. IGC

In the present study, IGC at infinite dilution was used to characterize the chemical surface of the polymeric resins. IGC is an accurate, reliable and quick method [7] and has frequently been applied for characterizing the surface of solid materials, such as polymers [8–12], carbons [13,14], aluminas [15] and some low cost adsorbents [16]. The method of IGC has been described in detail elsewhere [17,18] and only essential information is given below.

The free energy of adsorption, ΔG° (J/mol), is given by

$$\Delta G^\circ = -RT \ln(V_N) + C \quad (1)$$

where *R* is the ideal gas constant, *T* is the temperature of the system (K), *V_N* is the net retention volume (m³) and *C* is a constant that depends on the arbitrary chosen reference state of the adsorbate.

Dispersive and specific forces are considered to contribute independently to the interaction experienced between an adsorbate and an adsorbent, and therefore the free energy of adsorption may be split into dispersive (ΔG^d , J/mol), and specific (ΔG^s , J/mol) components:

$$\Delta G^s = \Delta G^\circ - \Delta G^d \quad (2)$$

For the non-polar *n*-alkane probes, it is assumed that there are no specific interactions, namely

$$\Delta G^\circ = \Delta G^d \quad (3)$$

For probes other than *n*-alkanes, the specific component of the free energy of adsorption, ΔG^s , could be evaluated as the vertical distance between the *n*-alkane reference line and the point on the diagram corresponding to the polar probe [19].

In the present IGC experiment, C₅–C₈ *n*-alkanes were selected as non-polar probe molecules, while acetone and benzene were selected as polar probe molecules. Measurements were carried out with a GC112 gas chromatograph (Shanghai Analytical Instrument General Factory, China) equipped with a flame ionization detector. A HW-2000 (Nanjing Qianpu Software Co., Ltd, China) software was applied for data acquisition and data analysis. Nitrogen was used as the carrier gas with a flow rate of 27 ml/min measured by a mass flow controller (Beijing Sevenstar Huachuang Electronic Co., Ltd, China). A 1 μ l Hamilton syringe was used to inject small amounts (0.1–0.3 μ l) of probe solutes. The stainless steel column was 3 mm inside diameter, and 30 cm in length. Column temperature was conditioned at 80 °C. Under these measurement conditions, symmetric chromatographic elution peaks were observed.

2.4. DRIFTS

In order to obtain more information concerning the surface functional groups of the resins, DRIFTS was carried out using a FT-IR spectrometer equipped with a diffuse reflectance attachment (Vector 33, Bruker). KBr was used as background for each sample.

2.5. Phenol adsorption experiments

Isotherms of phenol on the polymeric resins were separately estimated by the method of static adsorption. A detailed description of the procedure of the adsorption equilibrium experiments was given in our previous work [20].

3. Results and discussion

The porosity, the surface chemistry of the four polymeric resins and the phenol adsorption isotherms were investigated in this work. The experimental results were discussed in the following sections.

3.1. Textural properties

The textural parameters of the polymeric resins were obtained by nitrogen adsorption experiment at 77 K. Fig. 1 shows the nitrogen adsorption isotherms of the polymeric resins. According to IUPAC classification, pores within porous materials can be divided into micropore (width less than 20 Å), mesopore (width between 20 and 500 Å) and macropore (width greater than 500 Å). A distinct increase in nitrogen volume adsorbed at very low *P/P_o* (by the mechanism of micropore filling) indicated the presence of significant micropores in AB-8 and NKA-II resin, and a steep

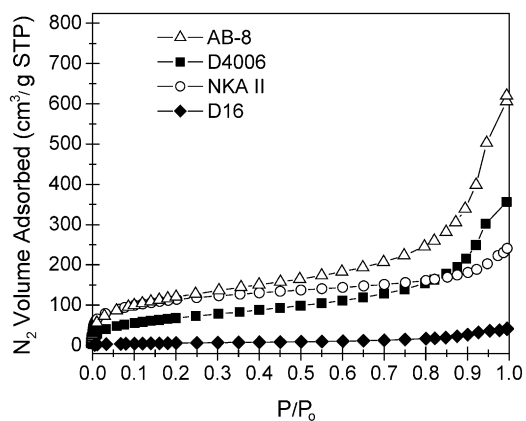


Fig. 1. Nitrogen adsorption isotherms at 77 K.

increase in nitrogen volume adsorbed at higher P/P_0 (by the mechanism of capillary condensation) suggested a relatively large contribution in mesopore and macropore range in AB-8 and D4006 resin. In the entire region of relative pressure, the nitrogen volume adsorbed was small for D16 resin, indicating a low porosity.

The structure parameters of the polymeric resins derived from the basis of the nitrogen adsorption data are summarized in Table 1.

Fig. 2 shows the DFT pore size distributions of the polymeric resins. Being different from the Barrett–Johner–Halenda (BJH) and Horvath–Kawazoe (HK) method based on classical theories, DFT is based on statistical mechanics [21]. What is more important, the DFT models cover a broad range of pore size (from micropore to macropore). As illustrated in Fig. 2, a peak in the micropore region was obviously observed in the PSD curves of NKA-II and AB-8 resin (at about 11 and 12 Å, respectively), while a distinct peak in the mesopore region could be seen in the PSD curves of AB-8 and D4006 resin (at about 210 Å). It meant that the micropores were dominant for NKA-II resin; the mesopores were dominant for AB-8 resin but there were also significant micropores in its structure; and the mesopores were dominant for D4006 resin. The relative flat shape of PSD curve of D16 resin indicated a low porosity. The different contribution to the porosity of the polymeric resins can also be explained by micropore volume and total pore volume as shown in Table 1. Among the four polymeric resins, AB-8 resin possessed the largest total pore volume, but NKA-II resin held the largest micropore volume.

Table 1
Porous structure parameters of polymeric resins

Resins	BET surface area (m ² /g)	BJH desorption average pore diameter (Å)	H-K median pore diameter (Å)	Micropore volume (cm ³ /g)	Total pore volume ^a (cm ³ /g)
AB-8	445	93.3	7.5	0.087	0.938
D4006	253	86.3	7.7	0.044	0.551
NKA-II	410	41.9	7.4	0.101	0.344
D16	22	46.8	9.3	0.003	0.058

^a at $P/P_0 = 0.98$.

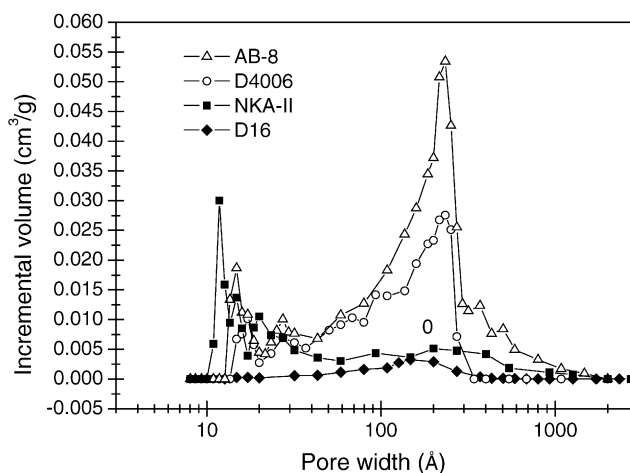


Fig. 2. DFT pore size distributions.

Based on the foregoing discussion, it can be concluded that there was a high development in the microporous structure in NKA-II and AB-8 resin, and an important development in the mesoporous structure in AB-8 and D4006 resin. The porosity of D16 resin, however, was very low compared to the other resins.

3.2. Chemical surface

IGC has been proved to be an ideally suited technique for the surface characterization of a wide range of materials [22]. In this study, IGC at infinite dilution was expected to provide the acid–base character and thus the information of the functionalities on the surface of the polymeric resins. The sample boiling point was used as the reference state in this work for experimental convenience similar to that described by Bailey et al. [17] and Dieckmann et al. [23] and $RT \ln(V_N)$ values vs. boiling temperatures of the respective probes were plotted. The plots for NKA-II resin are clearly shown in Fig. 3. The data of non-polar *n*-alkanes lie on a straight line (as the reference line) and the data of polar probes deviate from it. The deviations of the values of polar probes from the reference line correspond to the specific contributions of the free energy of adsorption.

It can be seen from Table 2 that the NKA-II resin exhibited an extraordinary high value of specific component compared to the other resins both in the case of polar probe acetone and benzene, indicating a surface of more strongly acidic or

Table 2

Measured value of the free energy of adsorption, calculated dispersion component and estimated specific component for polar probes at 353 K

Resins	Probes	Measured values $RT \ln(V_N)$ (kJ/mol)	Dispersion component $RT \ln(V_N^{REF})$ (kJ/mol)	Specific component ΔG^S (kJ/mol)
AB-8	Acetone	16.7	16.5	0.2
	Benzene	19.4	19.3	0.1
D4006	Acetone	17.1	16.8	0.3
	Benzene	22.0	19.9	0.1
NKA-II	Acetone	24.9	21.7	3.2
	Benzene	25.6	23.6	2.0
D16	Acetone	5.4	4.6	0.8
	Benzene	6.2	5.2	1.0

basic character. The specific components of AB-8 and D4006 both in the case of acetone and benzene were quite small, suggesting very weak surface polarity. The polarity of a resin could enhance its surface contact with aqueous solutions and thus the adsorption of phenol.

All the polymeric resins examined in this work, namely AB-8, D4006, NKA-II and D16 resin, were based on cross-linked polystyrene. Appropriate polar monomers were introduced into the polymeric network to obtain acidic or basic surface character. The results of IGC were well supported by DRIFTS spectra, as shown in Fig. 4. In all spectra there were peaks at 1502 and 2856 cm^{-1} corresponding to the C=C stretching vibration in aromatic rings and C–H stretching, respectively [24]. Intensive bands at 1755 and 1888 cm^{-1} were also observed for NKA-II resin, which could be associated with C=O stretching [25]. In Fig. 4, there were four other peaks present at 1718–1936 cm^{-1} for D16 resin, which resulted from C=O stretching and other functionalities.

3.3. Phenol adsorption isotherms

Fig. 5 shows the isotherms of phenol on the four kinds of polymeric resins at 295 K. It can be seen from Fig. 5 that the isotherm of phenol on NKA-II resin was the highest one. In comparison with AB-8 resin, although the micropore vol-

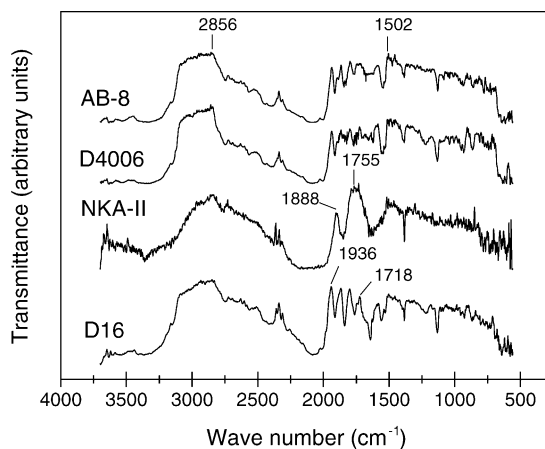


Fig. 4. DRIFTS spectra of samples.

ume of NKA-II resin was just slightly larger than that of AB-8 resin as shown in Table 1, the surface polarity of NKA-II resin was much stronger than that of AB-8 resin as shown in Table 2, which caused the adsorption capacity for phenol adsorbed on NKA-II resin was much higher than that on AB-8 resin. Trochimczuk et al. [6] had investigated the effects of some polar groups on polymer surface on the adsorptive properties toward phenol and pointed out that adsorption of phenol was stronger on adsorbents having more

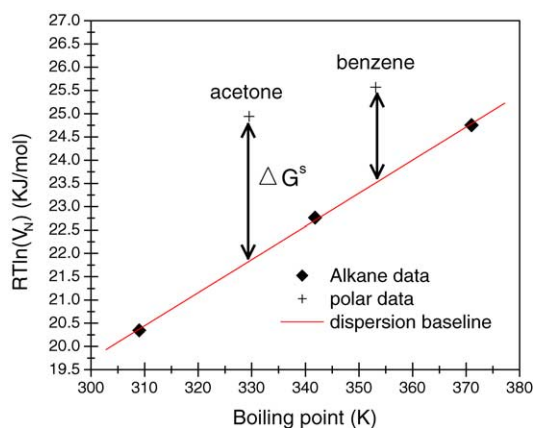


Fig. 3. Determination of the specific component of the free energy of adsorption for NKA-II resin.

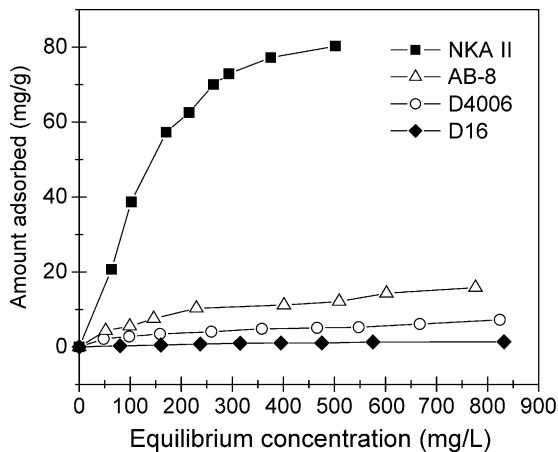


Fig. 5. Adsorption isotherms of phenol on different resins at 295 K.

polar groups. These groups caused an increase of surface polarity and hydrophilicity and then enhanced the adsorption of polar adsorbate (e.g. phenol). Fig. 5 also indicated that the isotherm of phenol on AB-8 resin was higher than that on D4006 resin. The reason was that the micropore volume of AB-8 resin was nearly two times of that of D4006 resin, while the surface polarity of AB-8 resin was nearly close to or slightly lower than that of D4006 resin, as shown separately in Tables 1 and 2. On the other word, this could be attributed to the micropore volume ($0.087 \text{ cm}^3/\text{g}$) of AB-8 resin as compared to that ($0.044 \text{ cm}^3/\text{g}$) of D4006 resin. If an adsorbent contained micropores, the potential fields from neighbouring walls will overlap and the interaction energy of the adsorbent with an adsorbate will be correspondingly enhanced [26]. In addition, it can be also seen that despite the stronger surface polarity of D16 resin in comparison with that of AB-8 resin, the isotherm of phenol on AB-8 resin was higher than that on D16 resin because the micropore volume of the AB-8 resin was much higher than that ($0.003 \text{ cm}^3/\text{g}$) of D16 resin. D16 resin was lack of porosity so that its specific surface area and micropore volume was very small. From the foregoing discussion, it can be concluded that the micropore volume and surface polarity were extremely significant for the adsorption of phenol on polymeric resins. The role of the stronger surface polarity of NKA-II resin was dominant for the adsorption of phenol in comparison with AB-8 resin since both of NKA-II resin and AB-8 resin had similar micropore volume. The role of the micropore volume of AB-8 resin was dominant for the adsorption of phenol in comparison with D4006 resin. Although D16 resin possessed relatively strong surface polarity, its micropore volume was so small that its adsorption capacity for phenol was the lowest.

4. Conclusion

From the foregoing discussion, the following conclusions can be available. The isotherm of phenol on NKA-II resin was the highest one due to its strongest surface polarity and largest micropore volume among the four kinds of resins. The isotherm of phenol on AB-8 resin was higher than that on D4006 since the micropore volume of AB-8 resin was nearly two times of that of D4006 resin. The micropore volume of D16 resin was so small that its adsorption capacity for phenol was the lowest although it possessed relatively strong surface polarity in comparison with AB-8 resin and D4006 resin. The experimental results suggested that adsorption of phenol on polymeric resins depended greatly on their microporosity

and surface chemistry. On the other word, the well-developed microporosity and the strong surface polarity would improve the adsorption of phenol on the polymeric resins.

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